"Green" Composites from Renewable Resources: Preparation of Epoxidized Soybean Oil and Flax Fiber Composites

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In recent years there has been considerable interest in using natural plant fibers as reinforcements for plastics. The motivation includes cost, performance enhancement, weight reduction, and environment concerns. High performance flax fiber could potentially substitute for glass or carbon fibers as reinforcements for plastics. This study reports the "green" composites obtained from a mixture of epoxidized soybean oil and epoxy resin, 1,1,1-tris(*p*-hydroxyphenyl)ethane triglycidyl ether (THPE-GE), reinforced with flax fiber. The compression molding method is used for making the composites. Curing agents triethylenetetramine and diethylenetriamine provide better physical properties of the composites than Jeffamine agents D-230 and EDR-148. Both the flexural modulus and the tensile modulus of the composites increase as the amount of THPE-GE increases. The flexural modulus increased at a fiber content of <10 wt %, but there is a decrease beyond 10 wt %. The tensile modulus increases with fiber content until a maximum at 13.5 wt %, and then it decreases. The flax fiber length affected the mechanical properties of the composites: the longer the fiber length, the better are the mechanical properties observed.

KEYWORDS: Epoxidized soybean oil; flax fiber; 1,1,1-tris(*p*-hydroxyphenyl)ethane triglycidyl ether (THPE-GE); composite

INTRODUCTION

During the past few years, there has been a growing interest in the use of polymers obtained from renewable resources because advantages of these polymers include their low production cost, in some cases, and their possible biodegradability (*1*). The importance of natural products for industrial applications also becomes very clear with increasing social emphasis on issues of the environment, waste disposal, and the depletion of nonrenewable resources. Significant amounts and varieties of plastics, such as polyolefins, polystyrene, and poly(vinyl chloride), are currently produced from fossil fuels, used, and then discarded into the environment, ending up as nondegradable wastes. Their disposal by incineration produces a net increase in carbon dioxide and, in some cases, toxic gases, which contribute to global pollution.

Among products from agricultural resources, natural oils may constitute raw materials useful in polymer synthesis. In the United States, the major source of vegetable oil for industrial application is soybean oil. For example, U.S. agriculture annually produces 1 billion pounds of soybean oil in excess of current commercial demand. This excess capacity has resulted in lower prices for soybean oil as well as other agricultural commodities. Development of economically feasible new industrial products from soybean oil or commercial processes is highly desirable. Biobased polymers are moving into the mainstream, and the polymers that are biodegradable or based on renewable "feedstock" may soon be competing with commodity plastics.

Seventy years ago, nearly all resources for the production of commodities and many technical products were materials derived from natural textiles. Textiles, ropes, canvas, and also paper were made of local natural fibers, such as flax and hemp. As early as 1908, the first composite materials were applied for the fabrication of large quantities of sheets, tubes, and pipes for electronic purposes (paper or cotton to reinforce sheets, made of phenol− or melamine−formaldehyde resins). In the early 20th century, for example, airplane seats and fuel tanks were made of natural fiber with a small content of polymeric binders (*2*). Owing to low prices and the steadily rising performance of technical and standard plastics, the application of natural fibers came to a near-halt. More recently, the critical discussion about the preservation of natural resources and recycling has led to a renewed interest in natural materials with the focus on renewable raw materials (*3*). So far, a good number of automotive components previously made with glass fiber composites are now being manufactured using environmentally friendly com-

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Scheme 1. Structure of THPE-GE
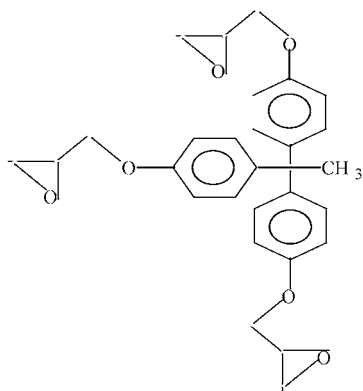
1,1,1-Tris(p-hydroxyphenyl)ethane triglycidyl ether (THPE-GE)

posites (*4*, *5*). A 50% growth in the use of natural fibers in the plastics industry is expected for 2000−2005 (*6*). The application of natural fibers in materials will be driven by environmental and economical concerns during the 21st century.

Flax has supplied fiber for textiles for thousands of years. Recently, flax has been considered to be a cost-effective alternative to glass in composites, because new technology and separation techniques have lowered the costs to produce fibers that are more uniform in color, strength, length, and fineness and thus better suited to composites (*7*). Replacing glass fibers with flax fibers in the composites may allow better materials separation, recycling, manufacturing, and reuse of production waste. End-of-life composite materials could be easily incinerated and used as an alternative fuel source with no glass residue. The low density values of plant fibers allow the production of composites that combine good mechanical properties with a low specific mass. A great deal of work has been published regarding the mechanical properties of plant fibers and how these fibers interact with various thermosets and thermoplastics (*8*−*10*). Wool and co-workers (*11*) reported the preparation of composites from plant oil based resin [acrylated epoxidized soybean oil (AESO)] and natural fiber mats made of flax, cellulose, pulp, and hemp. The composites with natural fiber reinforcement of ~10−50 wt % increased the flexural modulus to a range between 1.5 and 6 GPa depending on the nature of the fiber mat.

In our previous papers (*12*−*14*), we reported the preparation of epoxidized soybean oil based composites, reinforced with carbon, glass, and mineral fibers or with a combination of fiber and clay by extrusion solid freeform fabrication method. These polymeric composites demonstrate a variety of properties, ranging from elastomers to rigid plastics depending on the curing agents and epoxy resin (Epon 828) comatrix. The purpose of this work is to prepare epoxidized soybean oil based composites reinforced with flax fibers using a compression molding method. 1,1,1-Tris(*p*-hydroxyphenyl)ethane triglycidyl ether (THPE-GE), a new strong cross-linking or branching agent, is used as a comatrix, which is a reactive intermediate. THPE-GE can enhance key properties and improve the performance of the composites, for example, mechanical strength and heat or chemical resistance. The chemical structure of THPE-GE is shown in **Scheme 1**. The scanning electron microscopy (SEM) and mechanical (tensile and flexural strength) properties of the resulting composites were used to evaluate this research.

EXPERIMENTAL PROCEDURES

Materials. ESO (7.0% oxirane oxygen) was purchased from Alf Atochem Inc. (Philadelphia, PA). The resin used as a comatrix, THPE-

GE, was provided by the ChemFirst Co., Dallas, TX. Thixotropic agent, Aerosil R805, was obtained from Degussa Corp. (Ridgefield Park, NJ). Flax fibers are Dew-retted harvests (047FF VUB flax Dew-ratted, finest), provided by Russell Research Center, ARS, USDA, Athens, GA. The flax fibers were chopped into different fiber lengths using a Wiley mill, Digital-ED-5, model 3379K44 (Thomas Scientific, Swedesboro, NJ). Curing agents, 2,2′-(ethylenedioxy)bisethylamine (Jeffamine EDR-148) and polyalkyleneamine (Jeffamine D-230), were provided by Huntsman Corp. (Houston, TX) and used as received. Diethylenetriamine (DETA) and triethylenetetramine (TETA) 60% technical were purchased from Aldrich Chemical Inc. (Milwaukee, WI) and used without further purification.

Compression Molding. A conventional compression molding press (Carver Laboratory Press, model 2518.0221, Wabash, IN) with a maximum press capacity of 22 tons was used for test sample preparation. The molding temperature was 100 °C, and the force was 5000 lb.

Forming of Composites. ESO and THPE-GE were mixed well in the ratio of 1:0.33 (by weight) at 55 °C for 30 min. Vacuum was applied to remove air bubbles. The mixture was mixed with Aerosil R805, 8.83 g/100 g (ESO + THPE-GE) and degassed for 15 min at 55 °C. Designated flax fiber was added to the mixture with mechanical stirring for 15 min and degassed in a vacuum system at 55 °C for 30 min. The mixture was removed from the oven and cooled to room temperature, and curing agent was added with mechanical stirring. The mixture was transferred into the mold (115 × 115 × 3 mm) and degassed in a vacuum system at 55 °C for 30 min. Pressure was applied to the mold by a press at 5000 lb at 100 °C for 1 h. The mold was placed in an oven at 100 °C for 24 h for curing, and the molded sheet was knocked out and further cured at 140 °C for 48 h. The cured sample sheets were cut to 75 × 10 × 3 mm for mechanical testing.

SEM. SEM was performed to investigate the flax fiber and the interface between the filler and the polymeric matrix with a JEOLJSM 6400V instrument. The specimens were mounted on aluminum stubs with graphite-filled tape and vacuum-coated with gold−palladium on a JEOL ion sputter coater and observed. SEM micrographs were obtained using 5 kV of secondary electrons.

Mechanical Testing. *Tensile Tests.* The nonlinear mechanical behavior of the fibrous/soybean oil based composites was analyzed using an Instron model IX automated materials testing system in tensile mode, with a load cell of 1000 N capacity. The crosshead speed was 50 mm/min. The specimen was a thin rectangular strip (75 × 10 × 3 mm). Tensile tests were performed at 25 °C. Young's modulus (*E*) was measured from the low-strain region. The values reported in this study are the average of five measurements. Standard deviation range was ±5% on strength and modulus.

Bending Tests. Three-point bend tests were carried out at room temperature at a crosshead speed of 25 mm/min. Composites were tested using a span of 40 nm in an Instron model 1100. The standard formulas for the modulus, *E*, and strength, *σ*, in three-point bending of a beam are used:

$$E = PL^3/4bd^3\delta \qquad \sigma = 3PL/2bd^2$$

P is the break load, *L* is the support span, *δ* is the deformation at the center under load *P*, *d* is the sample height, and *b* is the sample width.

RESULTS AND DISCUSSION

Morphology. The SEM micrograph in **Figure 1** shows the structure of the flax fiber. **Figure 2** shows the SEM micrograph of the freshly fractured surface for a soybean oil based composite filled with flax fiber (fiber length = 3.63 mm). Fiber weight percentage is 10 wt %, using TETA curing agent. The micrograph clearly indicates a good interfacial adhesion between the fiber and matrix due to the physical contact between both components. The fibers are broken up from the matrix.

Effect of Curing Agent. Table 1 presents flexural strength and flexural modulus data for a composite consisting of ESO/THPE-GE in the ratio of 1:0.33 (by weight), flax fiber (fiber length = 3.62 mm), 10 wt %, Aerosil R805, 8.83 g/100 g (ESO
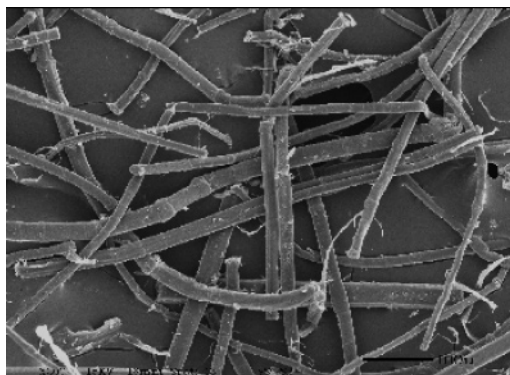
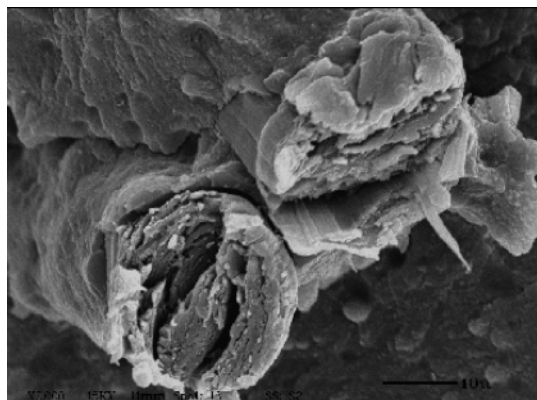**Figure 1.** Scanning electron micrograph of flax fiber.

Figure 2. Scanning electron micrograph of the freshly fractured surface of soybean oil-based composites filled with flax fiber.

Table 1. Effect of Curing Agents[a]

curing agent	flexural modulus (GPa)	flexural strength (MPa)	strain at break (%)
Jeffamine D-230	0.06	7.2	3.2
Jeffamine EDR-148	0.12	27.0	3.9
DETA	0.21	34.0	3.2
TETA	0.67	127	3.2

[a] Conditions: ESO/THPE-GE ratio, 1:0.33; flax fiber (3.62 mm), 10 wt %; Aerosil R805, 8.83 g/100 g (ESO + THPE-GE), and designated curing agent at ESO/H (amine) ratio of 1:1.67.

+ THPE-GE), and designated amount of curing agent. When Jeffamine D-230 was used as the curing agent, the composite had lower mechanical properties. This is presumably due to the reactivity of the amine groups in the Jeffamine D-230 (poly-oxypropylenediamine), where the amine groups are located on secondary carbon atoms at the ends of an aliphatic polyether chain. In contrast Jeffamine EDR-148, triethyleneglycoldiamine, amine groups are located on primary carbon atoms at the ends of an aliphatic polyether chain. Jeffamine EDR-148 is an unhindered diamine miscible in a wide variety of solvents. It is much more reactive than Jeffamine D-230. The reactivity of amines located on secondary carbon atoms is lower than that of amines located on primary carbon atoms. Because of this, the reactivity of Jeffamine EDR-148 is better than that of Jeffamine D230. On the other hand, TETA and DETA curing agents provide composites with better mechanical properties than those with Jeffamine agents because there are two primary amine groups located on primary carbon atoms at the ends of an aliphatic polyimine chain in TETA and DETA. At the same time, there is one secondary amine group in DETA and two secondary amine groups in TETA. These secondary amine

Table 2. Effect of ESO/THPE-GE Ratio[a]

ESO/THPE-GE ratio (wt)	flexural modulus (GPa)	flexural strength (MPa)	strain at break (%)
1:0.23	0.66	125	3.4
1:0.33	0.67	127	1.6
1:0.43	0.94	129	1.7

[a] Conditions: flax fiber (3.62 mm), 10 wt %; and Aerosil R805, 8.83 g/100 g (ESO + THPE-GE) using TETA curing agent at ESO/H (amine) ratio of 1:1.67.
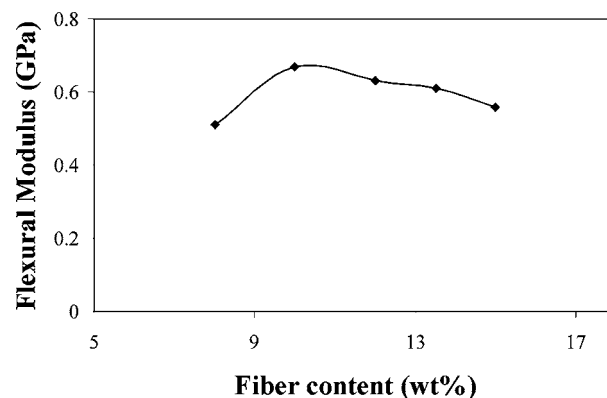

Figure 3. Flexural modulus of composites as a function of flax fiber content.

groups also take part in reactions and formulate a network structure of polymer matrix. The network structure of the polymer matrix provides stronger mechanical properties for composites.

Effect of ESO/THPE-GE Ratio. The experiments were carried out for investigating the influence of the ESO/THPE-GE ratio (by weight) on the mechanical properties of the composites. The results presented in **Table 2** show that flexural modulus increases as the THPE-GE concentration increases. This indicates that THPE-GE resin has a determining influence on the mechanical properties of the composites. In the two-component matrix system, ESO is a soft segment and THPE-GE resin is a hard segment. An increase in the THPE-GE resin concentration provides the composite with a higher flexural modulus.

Effect of Fiber Loading. At conditions of ESO/THPE-GE in the ratio of 1:0.33 (by weight), Aerosil R805, 8.83 g/100 g (ESO + THPE-GE), and TETA, 23.5 g/100 g (ESO + THPE-GE), the flexural modulus of composite as a function of flax fiber content is presented in **Figure 3**. It is observed that at the lower fiber content (up to 10 wt %) the flexural modulus increases but at a higher fiber content (up to 15 wt %) the flexural modulus shows a decrease. The best flexural properties are reached at ∼10 wt % fiber content. The Young's modulus as a function of fiber content is shown in **Figure 4**. A similar behavior is observed. The tensile modulus increases with fiber content until a maximum, at 13.5 wt %, and then it decreases with higher fiber loading. In the case of fiber-reinforced composites, it is well-known that there exits a critical aspect ratio at which the mechanical properties of the composites are maximized. This critical aspect ratio depends on the volume fraction of the fiber and also on the ratio of the modulus of fiber to matrix modulus (*15*). The decrease in the flexural properties at higher fiber contents is due to the increased fiber to fiber interactions and dispersion problems.

Influence of Fiber Length. Because of the discontinuous nature of the reinforcement, the tensile stress and stiffness of the composites are strongly influenced by the fiber length and
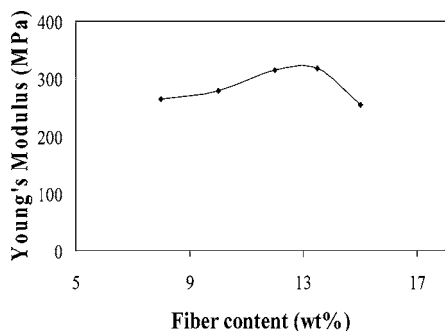
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Figure 4. Young's modulus of composites as a function of flax fiber content.

Table 3. Influence of Fiber Length

fiber length (mm)	tensile strength (MPa)	flexural strength (GPa)	tensile modulus (MPa)	flexural modulus (GPa)
0.5	8.14	0.083	144.05	0.276
1.0	8.95	0.097	157.20	0.300
2.0	10.30	0.100	166.76	0.484
3.6	10.40	0.127	278.82	0.668

its orientation. The flexural properties for the composites are also affected by the fiber length. The results of the tensile and flexural tests are given in **Table 3**. The highest tensile strength was observed for composites containing 3.62 mm flax fiber and the lowest tensile strength for those with 0.5 mm flax fiber. Tensile modulus was also higher in the composite with 3.62 mm fiber than in that with 0.5 mm flax fiber. The data of flexural strength and flexural modulus of the composites follow the same trend as the tensile data. The longer fibers give more strength to the composites than do shorter flax fibers.

Conclusions. From the above results the following conclusion maybe drawn. The biobased "green" composites have been developed from epoxidized soybean oil, THPE-GE, a comatrix resin, and flax fiber using a compression molding method. TETA and DETA curing agents provide better physical properties of the composites than do Jeffamine agents, D-230 and EDR-148. The flexural modulus and tensile modulus of these composites increased as the amount of THPE-GE increased. The flexural modulus also increased at a fiber content of <10 wt %, but there was a decrease beyond 10 wt %. The tensile modulus increased with fiber content until a maximum, at 13.5 wt %, and then it decreased. The flax fiber length affected the mechanical properties of the composites: the longer the fiber length, the better are the mechanical properties observed. The resulting composites had sufficient mechanical properties to be used in a wide variety of areas, such as agricultural equipment, civil engineering, and the automotive and construction industries.

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